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<b>(21) International Application Number:</b> PCT/US98/08863 <b>(22) International Filing Date:</b> 1 May 1998 (01.05.98)  <b>(30) Priority Data:</b> 60/045,632                      5 May 1997 (05.05.97)                      US 60/062,591                      20 October 1997 (20.10.97)                      US  <b>(71) Applicant:</b> EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US).  <b>(72) Inventors:</b> MCEL RATH, Kenneth, O.; 4314 Village Corner Drive, Houston, TX 77059 (US). TSE, Mun-Fu; 1706 Fair Oaks Drive, Seabrook, TX 77586 (US). TISLER, Andrew, L.; 1806 Threeflower Court, Kingwood, TX 77345 (US).  <b>(74) Agents:</b> PEEBLES, Brent, M. et al.; Exxon Chemical Com- pany, P.O. Box 2149, Baytown, TX 77522-2149 (US).		<b>(81) Designated States:</b> AT, BR, CA, CN, CZ, HU, JP, KR, MX, PL, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> COMPOSITION FOR TIRE SIDEWALLS AND OTHER RUBBER CONSTRUCTIONS		
<b>(57) Abstract</b>  Rubber blends of brominated isobutylene/para-methylstyrene copolymers of 9.5 to 20 weight percent aromatic monomer content and 0.2 to 1.0 mole percent benzylic bromine content. The blends have good cure characteristics, good adhesion and flex crack resistance, as well as ozone resistance. The blends are useful in tire sidewalls, and other applications.		

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**COMPOSITION FOR TIRE SIDEWALLS  
AND OTHER RUBBER CONSTRUCTIONS**

This is based on Provisional Applications USSN 60/045,632 filed May 5, 1997,  
5 and USSN 60/062,591 filed October 20, 1997

**FIELD OF THE INVENTION**

The present invention relates to compositions for making tire sidewalls and other rubber constructions which exhibit improved ozone resistance and fatigue  
10 crack propagation resistance, as well as a reduction in staining and discoloration. The composition comprises a blend of halogenated copolymer of isoolefin and para-alkylstyrene of relatively high aromatic comonomer content and relatively low halogen content with general purpose rubbers (GPR) such as butadiene rubber (BR), natural rubber (NR) and/or isoprene rubber (IR). The tire sidewall may  
15 comprise a single layer or a veneer construction wherein an outer layer comprises the blend of the halogenated copolymer with one or more general purpose rubbers, and an inner layer can comprise a blend of general purpose rubbers.

**BACKGROUND OF THE INVENTION**

20 Rubber tires, such as pneumatic tires, include many components, such as, for example, sidewalls. Sidewalls are continuously subjected to distortion under normal road operating conditions. The sidewalls are subjected to extensive continuous flexing and can crack under such conditions. In addition to flex cracking, sidewalls are also subjected to atmospheric chemical action such as  
25 ozone attack. The overall effect is that the sidewalls may erode and degrade. The sidewall may even separate from the tire carcass during use, leading to tire failure.

To reduce the problems caused by ozone attack and flex cracking, tire manufacturers add chemical protectants to the general purpose rubbers used in tire sidewalls. The problem with these protectants is that they tend to be fugitive and  
30 can cause staining when in contact with white sidewalls. In some cases,

particularly in white sidewalls, polymer blends have been used to effect improvements in ozone and flex resistance.

Published International application PCT/US91/05666 filed Aug. 9, 1991 discloses a tire sidewall composition comprising a single layer prepared from a blend of a halogenated copolymer of isoolefin and para-alkylstyrene with one or more general purpose rubbers.

U.S. Patent 5,376,438 to Costemalle et al. discloses multi-layer tire sidewalls having an outer layer prepared from a blend of halogenated isomonoolefin/para-alkylstyrene copolymer and general purpose rubbers. The inner layer comprises general purpose rubber. The sidewalls are said to exhibit good ozone resistance and fatigue crack resistance as well as a reduction in staining and discoloration. This patent is hereby incorporated herein by reference in its entirety.

In the prior art, the halogen content of the halogenated isoolefin/para-alkylstyrene copolymers generally varied proportionately with the para-alkylstyrene content, e.g. higher para-methylstyrene content was used to get a higher halogen content. If the copolymer was excessively halogenated, some undesirable dihalo benzylic substitution would occur. Thus, excess para-methylstyrene was usually used. In tire sidewall compositions of the prior art, a relatively high bromine level was needed to achieve adhesion and ozone resistance, but such high bromination levels led to relatively tight cures and crack propagation. It would be desirable to be able to use a rubber blend of the halogenated isoolefin/para-alkylstyrene copolymer that has both good adhesion and ozone resistance, as well as flex crack resistance and cure properties.

#### SUMMARY OF THE INVENTION

It has been found that the use of blends of halogenated copolymers of isoolefin and para-alkylstyrene having specific contents of aromatic monomers and halogenation, with general purpose rubbers yield tire sidewall compositions having significantly improved ozone resistance and fatigue crack propagation resistance. It has now been discovered that excellent curing and crack propagation resistance can

be achieved simultaneously with good adhesion and ozone resistance by using a relatively low halogenation content in combination with a relatively high aromatic or para-alkylstyrene content.

In one aspect, the invention is a blend of rubber and a brominated copolymer of an isoolefin and a para-alkylstyrene. The copolymer comprises at least 9.5 but less than 20 weight percent of aromatic monomers (styrenics), and at least 0.2 but less than 1 mole percent para-bromoalkylstyrene. The blend preferably comprises from 35 to 65 phr of the copolymer, and from 35 to 65 phr of the general purpose rubber. The styrenics can include para-alkylstyrene, brominated para-alkylstyrene, alpha-methylstyrene, brominated alpha-methylstyrene or combinations thereof. The isoolefin is preferably isobutylene, whereas the para-alkylstyrene is preferably para-methylstyrene and the para-bromoalkylstyrene is preferably para-bromomethylstyrene. The general purpose rubber can be a natural rubber, styrene-butadiene rubber, polybutadiene rubber and combinations thereof. The copolymer preferably comprises from 12 to 17 weight percent unbrominated styrenics, and from 0.4 to 0.8 mole percent para-bromoalkylstyrene.

In another aspect, the invention provides a tire sidewall comprising a layer of the blend described above. The blend can also be used in a veneered tire sidewall wherein an outer layer comprises the blend described above, and an inner layer comprises a highly unsaturated rubber or blend of unsaturated rubbers.

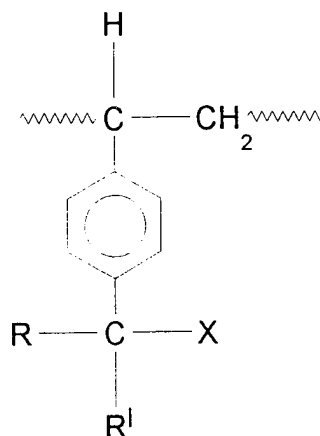
In a further aspect, the invention provides an improvement in a tire sidewall comprising at least an outer layer comprising a blend of a copolymer of an isoolefin and a para-alkylstyrene and an unsaturated rubber, and an inner layer optionally comprising a highly saturated rubber or blend of unsaturated rubbers. The improvement is that the copolymer comprises from 9.5 to 20 weight percent aromatic monomers and from 0.2 to 1.0 mole percent para-bromoalkylstyrene.

Preferably, the blend contains quantities of bromoalkylstyrene and para-alkylstyrene which satisfy the following formula:

$$X = [1.91 - (0.094 \times Y)] \pm 0.1$$

where "X" is mole percent bromoalkylstyrene and "Y" is weight percent para-alkylstyrene (between the proposed limits of 9.5 to 20 weight percent). " $\pm 0.1$ " as used herein indicates that the value X may be any number within the range of 0.1 above to 0.1 below  $[1.91 - (0.094 \times Y)]$ . The bromoalkylstyrene is preferably para-bromomethylstyrene and the para-alkylstyrene is preferably para-methylstyrene. More preferably, the blend of the present invention has 0.96 mole percent para-bromomethylstyrene and 10 weight percent para-methylstyrene. Alternatively, the blend of the present invention preferably has 0.84 mole percent para-bromomethylstyrene and 12.5 weight percent para-methylstyrene.

In the preferred embodiment, the polymerized para-alkylstyrene comonomer unit is characterized by the formula:



wherein R and R<sup>1</sup> are independently selected from the group consisting of hydrogen, alkyl groups having from 1 to about 5 carbon atoms, and primary and secondary alkyl halides having from 1 to about 5 carbon atoms, and X is selected from the halogen group consisting primarily of bromine, chlorine and mixtures thereof. Furthermore, the halogenated para-alkylstyrene unit is shown as being pendant from the isoolefin polymer chain, represented by the wavy lines in the formula.

The tire sidewall composition and layers of the present invention can be compounded by methods generally known in the art, such as by mixing with the

uncured polymers various fillers such as titanium dioxide; carbon black, when black sidewalls are desired, or non-black fillers and pigments; extenders such as rubber process oils; curing aids such as zinc oxide, sulfur; accelerators or retarders and other additives such as antioxidants and antiozonants.

5

#### DETAILED DESCRIPTION OF THE INVENTION

The principal advantages realized by practice of the present invention primarily stem from the fact that by employing a blend of copolymer of an isoolefin and para-alkylstyrene with general purpose rubbers (GPR), wherein the copolymer has a low halogen content but high aromatics content, superior ozone resistance and flex fatigue crack resistance and adhesion can be achieved at the same time.

The invention in one embodiment involves the construction of a multi-layered tire sidewall, the outer layer of which comprises a blend of a copolymer of an isoolefin and para-alkylstyrene with one or more unsaturated rubbers (GPR). The sidewall also comprises one or more layers constructed from conventional sidewall compositions such as those discussed in "The Vanderbilt Rubber Handbook" pp. 605 (1990).

The outer layer of the sidewall is fabricated from a blend composition comprising at least one highly unsaturated rubber selected from the group consisting of natural rubber, SBR rubber, polyisoprene and polybutadiene rubber; and a halogenated copolymer of an isoolefin and a para-alkylstyrene unit. In a particularly preferred composition useful in tire sidewalls, the halogenated copolymer comprises about 35 to 65 parts, for example, 40 parts, and the unsaturated rubber desirably comprises from 35 to 65 parts natural rubber and/or polybutadiene rubber. The outer layer blend may also optionally include from about 1 to about 90 preferably from about 5 to about 20 parts per hundred of ethylene-propylene-diene rubber (EPDM). The highly unsaturated rubber component of the outer layer may consist of a blend or mixture of two or more highly unsaturated rubbers. These optional rubbers may also contain aromatic monomers to improve their compatibility.

When white sidewalls are desired, particularly preferred outer layer compositions comprise the halogenated para-alkylstyrene copolymer and natural rubber in a weight ratio of halogenated para-alkylstyrene copolymer to natural rubber ranging from about 0.28:1 to about 3:1, preferably about 0.67:1 to about 1:1. The preferred halogenated para-alkylstyrene copolymer for white sidewall outer layers comprises preferably from about 9.5 to 20, more preferably from about 12 to about 17 weight percent para-alkylstyrene moieties and preferably from about 0.2 to about 1.0 mole percent, more preferably 0.4 to 0.8 mole percent halogenated para-alkylstyrene.

In a multi-layered construction, the inner layer or layers comprise one or more unsaturated rubbers selected from the group comprising natural rubber, styrene butadiene rubber, polybutadiene rubber. Typically such compositions comprise blends of natural rubber and polybutadiene rubber or blends of styrene butadiene rubber and polybutadiene rubber. The inner layer may also comprise fillers such as oils and antiozonants and other additives well known in the art.

The highly unsaturated rubbers are selected from the group consisting of natural rubbers, polyisoprene rubbers, styrene butadiene rubber (SBR) and polybutadiene rubber and mixtures thereof. The natural rubbers are selected from the group consisting of Malaysian rubber such as SMR CV, SMR 5, SMR 10, SMR 20, and SMR 50 and mixtures thereof, wherein the natural rubbers have a Mooney viscosity at 100° C (ML 1+4) of about 30 to about 120, more preferably about 40 to about 65. Comparable Indonesian rubbers, with SIR pre-fixes, may also be used. The Mooney viscosity test referred to herein is in accordance with ASTM D-1646.

The Mooney viscosity of the polybutadiene rubber as measured at 100° C (ML 1+4) may range from about 40 to about 70, more preferably about 45 to about 65, and most preferably about 50 to about 60. When both natural rubber and polybutadiene rubber are used, ranges from about 100 to 1 to 1 to 100, more preferably 5 to 1 to 1 to 5, and most preferably 2 to 1 to 1 to 2 are suggested.

EPDM is the ASTM designation for a terpolymer of ethylene, propylene and a non-conjugated diolefin. In such terpolymers the ethylene and propylene

form a fully saturate backbone of methylene linkages with the non-conjugated diolefin, e.g. dicyclopentadiene or substituted norbornene, attached so as to provide unsaturated side chains with readily available crosslinking sites for sulfur curing. The EPDM elastomers thus contain a fully saturated backbone which provides outstanding resistance to oxidation, ozone, and cracking, as well as excellent low temperature flexibility. The Mooney viscosity of the EPDM terpolymer as measured at 125° C is about 20 to 80, more preferably about 25 to 75 and most preferably about 40 to about 60. The ethylene content of the EPDM terpolymers may range from about 20 to about 90 weight percent, preferably from about 30 to about 85, more preferably from about 35 to about 80 weight percent. The total diene monomer content in the EPDM terpolymers may suitably range from about 0.1 to about 15 weight percent, preferably from about 0.5 to about 12 weight percent.

The non-conjugated dienes may be straight chain or cyclic hydrocarbon diolefins having from 6 to 15 carbon atoms, such as dicyclopentadiene, including 5-methylene-2-norbornene, 5-vinyl-2-norbornene, 2-methylnorbornadiene, 2, 4-dimethyl-2,7-octadiene, 1,4-hexadiene and 5-ethylidene-2-norbornene. The more preferred compounds include 5-methylene-2-norbornene, dicyclopentadiene, 1,4-hexadiene and 5-ethylidene-2-norbornene. A preferred EPDM terpolymer is VISTALON® 6505 manufactured by Exxon Chemical Company.

The term "butyl rubber" as employed herein is intended to refer to a vulcanizable rubbery copolymer containing, by weight, from about 85 to 99.5% combined isoolefin having from 4 to 8 carbon atoms. Such copolymers and their preparation are well known. The butyl rubber may be halogenated by means known in the art. The Mooney viscosity of the halobutyl rubbers useful in the instant invention are measured at 125 ° C. (ML 1+4) range from about 20 to about 80, more preferably about 25 to about 55, and most preferably about 30 to about 50.

Suitable halogen-containing copolymers of a C<sub>4</sub> to C<sub>7</sub> isomonoolefin and a para-alkylstyrene for use as a component of the present blends and tire sidewall

compositions comprise at least 9.5 weight percent of the para-alkylstyrene moiety. For elastomeric copolymer products, the para-alkylstyrene moiety may range from about 9.5 weight percent to about 20 weight percent, preferably from about 12 to about 17 weight percent of the copolymer. The halogenated content of the copolymers may range from about 0.2 to about 1.0 mole percent, preferably from about 0.4 to about 0.8 mole percent. The halogen may be bromine, chlorine and mixtures thereof. Preferably, the halogen is bromine. The major portion of the halogen is chemically bound to the para-alkyl group, that is, the halogen-containing copolymer comprises para-haloalkyl groups.

The copolymers of the isomonoolefin and para-alkylstyrene useful to prepare the halogen-containing copolymers suitable as a component of the tire sidewall composition of the present invention include copolymers of isomonoolefin having from 4 to 7 carbon atoms and a para-alkylstyrene, such as those described in U.S. Pat. No. 5,162,445. The preferred isomonoolefin comprises isobutylene. The preferred para-alkylstyrene comprises para-methylstyrene. Other aromatic monomers and styrenics, for example, alkylstyrenes such as alpha-methylstyrene and meta-methylstyrene, may be employed in lieu of some of the para-alkylstyrene, provided the total aromatic content of the copolymer is in the range of 9.5 to 20 weight percent, preferably 12 to 17 weight percent. Sufficient amounts of the para-alkylstyrene must, of course, be used to obtain the halogenated copolymer with the halogenated para-alkyl groups.

Preferably, the blend of the present invention contains quantities of bromoalkylstyrene and para-alkylstyrene which satisfy the following formula:

$$X = [1.91 - (0.094 \times Y)] \pm 0.1$$

where "X" is mole percent bromoalkylstyrene and "Y" is weight percent para-alkylstyrene (between the limits of 9.5 to 20 weight percent). " $\pm 0.1$ " as used herein indicates that the value X may be any number within the range of 0.1 above to 0.1 below  $[1.91 - (0.094 \times Y)]$ . The bromoalkylstyrene is preferably para-bromomethylstyrene and the para-alkylstyrene is preferably para-methylstyrene. More preferably, the blend of the present invention has 0.96 mole percent para-

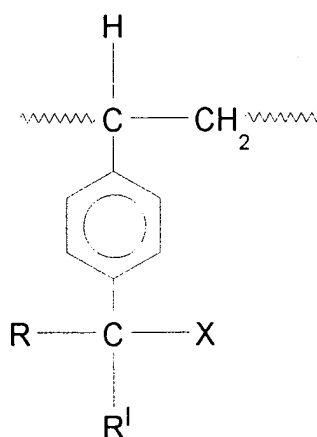
bromomethylstyrene and 10 weight percent para-methylstyrene. Alternatively, the blend of the present invention preferably has 0.84 mole percent para-bromomethylstyrene and 12.5 weight percent para-methylstyrene.

Suitable copolymers of an isomonoolefin and a para-alkylstyrene include  
5 copolymers having a weight average molecular weight ( $M_w$ ) of at least about 100,000, preferably at least about 300,000, and a number average molecular weight ( $M_n$ ) of at least about 100,000. The copolymers also, preferably, have a ratio of weight to number average molecular weight, i.e.,  $M_w/M_n$  of less than about 6 preferably less than about 4. The brominated copolymer of the isoolefin  
10 and para-alkylstyrene obtained by the polymerization of these particular monomers under certain specific polymerization conditions now permits one to produce copolymers which comprise the direct reaction product (that is, in their as-polymerized form), and which have unexpectedly homogeneous uniform compositional distributions. Thus, by utilizing the polymerization and bromination  
15 procedures set forth herein, the copolymers suitable for the practice of the present invention can be produced. These copolymers, as determined by gel permeation chromatography (GPC) demonstrate narrow molecular weight distributions and substantially homogeneous compositional distributions, or compositional uniformity over the entire range of compositions thereof. At least about 95 weight  
20 percent of the copolymer product has a para-alkylstyrene content within about 7 weight percent, of the average para-alkylstyrene content for the overall composition, and preferably at least about 97 weight percent of the copolymer product has a para-alkylstyrene content within about 7 weight percent, of the average para-alkylstyrene content for the overall composition. This substantially  
25 homogeneous compositional uniformity thus particularly relates to the intercompositional distribution. That is, with the specified copolymers, as between any selected molecular weight fraction the percentage of para-alkylstyrene therein, or the ratio of para-alkylstyrene to isoolefin, will be substantially the same, in the manner set forth above.

30 In addition, since the relative reactivity of para-alkylstyrene with isoolefin such as isobutylene is close to one, the intercompositional distribution of these

copolymers will also be substantially homogeneous. That is, these copolymers are essentially random copolymers and in any particular polymer chain the para-alkylstyrene and isoolefin units will be essentially randomly distributed throughout the chain.

5 The halogen-containing copolymers useful in the practice of the present invention have a substantially homogenous compositional distribution and include the para-alkylstyrene moiety represented by the formula:



10 in which R and R<sup>1</sup> are independently selected from the group consisting of hydrogen, alkyl preferably having from 1 to 5 carbon atoms, primary haloalkyl, secondary haloalkyl preferably having from 1 to 5 carbon atoms, and mixtures thereof and X is selected from the group consisting of bromine, chlorine and  
15 mixtures thereof, such as those disclosed in U.S. Pat. No. 5,162,445, the teachings of which are incorporated by reference.

Various methods may be used to produce the copolymers of isomonoolefin and para-alkylstyrene, as known in the art. Preferably, the polymerization is carried out continuously in a typical continuous polymerization process using a  
20 baffled tank-type reactor fitted with an efficient agitation means such as a turbo mixer or propeller, and draft tube, external cooling jacket and internal cooling coils or other means of removing the heat of polymerization, inlet pipes for monomers, catalyst and diluents, temperature sensing means and an effluent overflow to a holding drum or quench tank. The reactor is purged of air and moisture and

charged with dry, purified solvent or a mixture of solvent prior to introducing monomers and catalysts.

Reactors which are typically used in butyl rubber polymerization are generally suitable for use in polymerization reaction to produce the desired para-alkylstyrene copolymers suitable for use in the present invention. The polymerization temperature may range from about minus 35° C to about minus 100° C, preferably from about minus 40° to about minus 80° C.

The processes for producing the copolymers can be carried out in the form of a slurry of polymer formed in the diluents employed, or as a homogeneous solution process. The use of a slurry process is, however, preferred, since in that case, lower viscosity mixtures are produced in the reactor and slurry concentrations of up to 40 weight percent of polymer are possible. However, a solution process is preferred for the higher levels of PMS.

The copolymers of isomonoolefins and para-alkylstyrene may be produced by admixing the isomonoolefin and the para-alkylstyrene in a copolymerization reactor under copolymerization conditions in the presence of a diluent and a Lewis acid catalyst.

Typical examples of the diluents which may be used alone or in a mixture include propane, butane, pentane, cyclopentane, hexane, toluene, heptane, isooctane, etc., and various halohydrocarbon solvents which are particularly advantageous herein, including methylene chloride, chloroform, carbon tetrachloride, and methyl chloride, with methyl chloride being particularly preferred.

An important element in producing the copolymer is the exclusion of the impurities from the polymerization reactor, namely, impurities which if present, will result in complexing with the catalyst or copolymerization with the isomonoolefins or the para-alkylstyrene, which in turn will prevent one from producing the para-alkylstyrene copolymer product useful in the practice of the present invention. Most particularly, these impurities include the catalyst poisons, moisture and the like. These impurities should be kept out of the system.

In producing the suitable copolymers, it is preferred that the para-alkylstyrene be at least 95.0 weight percent pure, preferably 97.5 weight percent pure, most preferably 99.5 weight percent pure, that the isomonoolefin be at least 99.5 weight percent pure, preferably at least 99.8 weight percent pure, and that the diluents employed be at least 99 weight percent pure, and preferably at least 99.8 weight percent pure.

The most preferred Lewis acid catalysts are ethyl aluminum dichloride and preferably mixtures of ethyl aluminum dichloride with diethyl aluminum chloride. The amount of such catalysts employed will depend on the desired molecular weight and the desired molecular weight distribution of the copolymer being produced, but will generally range from about 20 ppm to 1 weight percent and preferably from about 0.001 to 0.2 weight percent based upon the total amount of monomer to be polymerized.

Halogenation of the polymer can be carried out in the bulk phase (e.g. melt phase) or either in solution or in a finely dispersed slurry. Bulk halogenation can be effected in an extruder, or other internal mixer, suitably modified to provide adequate mixing and for handling the halogen and corrosive by-products of the reaction. The details of such bulk halogenation processes are set forth in U.S. Pat. No. 4,548,995, which is hereby incorporated by reference.

Suitable solvents for solution halogenation include the low boiling hydrocarbons ( $C_4$  to  $C_7$ ) and halogenated hydrocarbons. Since the high boiling point para-methylstyrene makes its removal by conventional distillation impractical, and since it is difficult to completely avoid solvent halogenation, it is very important where solution or slurry halogenation is to be used that the diluent and halogenation conditions be chosen to avoid diluent halogenation, and that residual para-methylstyrene has been reduced to an acceptable level.

With halogenation of para-methylstyrene/isobutylene copolymers, it is possible to halogenate the ring carbons, but the products are rather inert and of little interest. However, it is possible to introduce halogen desired functionality into the para-methylstyrene/isobutylene copolymers hereof in high yields and under

practical conditions without obtaining excessive polymer breakdown, cross-linking or other undesirable side reactions.

It should be noted that radical bromination of the enchaind para-methylstyryl moiety in the useful copolymers for the practice of this invention can be made highly specific with almost exclusive substitution occurring on the para-methyl group, to yield the desired benzylic bromine functionality. The specificity of the bromination reaction can thus be maintained over a broad range of reaction conditions, provided, however, the factors which would promote the ionic reaction route are avoided (i.e., polar diluents, Friedel-Crafts catalysts, etc.).

Thus, solutions of the suitable para-methylstyrene/isobutylene copolymers in hydrocarbon solvents such as pentane, hexane or heptane can be selectively brominated using light, heat, or selected radical initiators (according to conditions, i.e., a particular radical initiator must be selected which has an appropriate half-life for the particular temperature condition being utilized, with generally longer half-lives preferred at warmer halogenation temperatures) as promoters of radical halogenation, to yield almost exclusively the desired benzylic bromine functionality, via substitution on the para-methyl group, and without appreciable chain scission and/or crosslinking.

This reaction can be initiated by formation of a bromine atom, either photochemically or thermally (with or without the use of sensitizers), or the radical initiator used can be one which preferentially reacts with a bromine molecule rather than one which reacts indiscriminately with bromine atoms, or the solvents or polymer (i.e., via hydrogen abstraction). The sensitizers referred to are those photochemical sensitizers which will themselves absorb lower energy photons and disassociate, thus causing in turn, disassociation of the bromine, including materials such as iodine. It is, thus, preferred to utilize an initiator which has a half life of between about 0.5 and 2500 minutes under the desired reaction conditions, more preferably about 10 to 300 minutes. The amount of initiator employed will usually vary between 0.02 and 1 percent by weight on the copolymer, preferably between about 0.02 and 0.3 percent. The preferred initiators are bis azo compounds such as azo bis isobutyronitrile (AIBN), azo bis(2,4-dimethylvalero)nitrile, azo bis(2-

methylbutyro)nitrile, and the like. Other radical initiators can also be used, but it is preferred to use a radical initiator which is relatively poor at hydrogen abstraction, so that it reacts preferentially with the bromine molecules to form bromine atoms rather than with the copolymer or solvent to form alkyl radicals. In those cases, there would then tend to be resultant copolymer molecular weight loss, and promotion of undesirable side reactions, such as crosslinking. The radical bromination reaction of the copolymers of para-methylstyrene and isobutylene is highly selective, and almost exclusively produces the desired benzylic bromine functionality. Indeed, the only major side reaction which appears to occur in disubstitution at the para-methyl group to yield the dibromo derivative, but even this does not occur until more than about 60 percent of the enchaind para-methylstyryl moieties have been monosubstituted. Hence, any desired amount of benzylic bromine functionality in the monobromo form can be introduced into the above stated copolymers, up to about 60 mole percent of the para-methylstyrene content. Stated differently the para-methylstyrene content should preferably be at least twice the desired para-bromomethylstyrene content to avoid dibromination.

It is desirable that the termination reactions be minimized during bromination, so that long, rapid radical chain reactions occur, and so that many benzylic bromines are introduced for each initiation, with a minimum of the side reactions resulting from termination. Hence, system purity is important, and steady-state radical concentrations must be kept low enough to avoid extensive recombinations and possible crosslinking. The reactions must also be quenched once the bromine is consumed, so that continued radical production with resultant secondary reactions (in the absence of bromine) do not then occur. Quenching may be accomplished by cooling, turning off the light source, adding dilute caustic, the addition of a radical trap, or combinations thereof.

Since one mole of HBr is produced for each mole of bromine reacted with or substituted on the enchaind para-methylstyryl moiety, it is also desirable to neutralize or otherwise remove this HBr during the reaction, or at least during polymer recovery in order to prevent it from becoming involved in or catalyzing

undesirable side reactions. Such neutralizations and removal can be accomplished with a post-reaction caustic wash, generally using a molar excess of caustic on the HBr. Alternatively, neutralization can be accomplished by having a particulate base (which is relatively nonreactive with bromine) such as calcium carbonate powder present in dispersed form during the bromination reaction to absorb the HBr as it is produced. Removal of the HBr can also be accomplished by stripping with an inert gas (e.g., N<sub>2</sub>) preferably at elevated temperatures.

The brominated, quenched, and neutralized para-methylstyrene/isobutylene copolymers can be recovered and finished using conventional means with appropriate stabilizers being added to yield highly desirable and versatile functional saturated copolymers.

In summary, halogenation to produce a copolymer useful in the present invention is preferably accomplished by halogenating an isobutylene-para-methylstyrene copolymer using bromine in a normal alkane (e.g., pentane, hexane or heptane) solution utilizing a bis azo initiator, e.g., AIBN or VAZO® 52: 2,2'-azobis(2,4-dimethyl-pentane nitrile), at about 55° to 80° C, for a time period ranging from about 4.5 to about 30 minutes, followed by a caustic quench. The halogen content is generally controlled by limiting the quantity of halogen reactant. The recovered polymer is washed in basic water and water/isopropanol washes, recovered, stabilized and dried.

The aromatic halomethyl groups permit facile crosslinking to be accomplished in a variety of ways, for example, either directly through the halomethyl group or by conversion to other functional groups, as indicated above, to permit the desired crosslinking reactions to be employed. Direct crosslinking can be effected with a variety of polyfunctional groups, as indicated above, to permit the desired crosslinking reactions to be employed. Direct crosslinking can be effected with a variety of polyfunctional nucleophilic reagents such as ammonia, amines, or polyamines; metal dicarboxylates; metal dithiolates; promoted metal oxides (e.g., ZnO+zinc stearates and/or dithiocarbamates), etc. Crosslinking can also be effected via polyalkylation reactions. The aromatic halomethyl groups thus provide a wide choice of crosslinking reactions which can be used.

Various fillers can also be used in single layer or the outer and/or inner layer blend compositions of the present invention, and these include a variety of carbon blacks, clays, silicas, carbonates, oils, resins, and waxes. Carbon blacks preferred for use in black tire sidewall compositions of this invention include those types designated N339, N774, N660, N351 and N375. Alternatively, non-black fillers and pigments may be used for white tire sidewalls. The blends are cured with conventional curatives for highly unsaturated or chlorobutyl rubbers, including sulfur, alkylphenol disulfide, zinc oxide, sulfenamide derivatives, guanidines, benzothiazyl disulfide (MBTS) and mercaptobenzothiazole (MBT).

When constructing tires employing the sidewalls of the invention, the sidewalls can be made of the blend composition, or the present blend composition can be used as an outer layer or veneer over an inner layer. The thickness of the inner and outer layers will vary depending upon the type and size of the tires being built. Typically for a passenger car tire, the outer layer thickness may vary from about 0.8 mm to about 2.0 mm. The inner layer may vary from about 1.0 mm to about 2.0 mm. For example, a tire size 185/60-HR-14 would have a sidewall width of about 95 mm and an overall length of about 1210 mm.

The single-layer or multi-layered tire sidewall compositions of the present invention may be vulcanized by subjecting them to heat and/or light or radiation according to any vulcanization process.

The single-layer or multi-layered tire sidewall of the present invention may be used as the sidewall for motor vehicle tires such as truck tires, bus tires, passenger automobile, motorcycle tires and the like.

Suitable tire sidewall layer compositions may be prepared by using conventional mixing techniques including, e.g., kneading, roller milling, extruder mixing, internal mixing (such as with a Banbury® mixer), etc. The sequence of mixing and temperatures employed are well known to the skilled rubber compounder, the objective being the dispersion of fillers, activators and curatives in the polymer matrix without excessive heat buildup. A useful mixing procedure utilizes a Banbury mixer in which the rubber components, fillers, and plasticizer are added and the composition mixed for the desired time to a particular temperature

to achieve adequate dispersion of the ingredients. Alternatively, the rubbers and a portion of the fillers (e.g., one-third to two-thirds) is mixed for a short time (e.g. about 1 to 3 minutes) followed by the remainder of the fillers and oil. Mixing is continued for about 5 to 10 minutes at high rotor speed during which time the mixed components reach a temperature of about 150° C. Following cooling, the components are mixed in a second step on a rubber mill or in a Banbury mixer during which the curing agent and optional accelerator, are thoroughly and uniformly dispersed at a relatively low temperature, e.g., about 80° to about 105° C. Variations in mixing will be readily apparent to those skilled in the art and the present invention is not limited to any specific mixing procedure. The mixing is performed to disperse all components of the composition thoroughly and uniformly.

Tires are generally built on a drum from at least three layers, namely, an outer layer comprising a tread portion and sidewalls comprising the inner and outer layers of this invention, an intermediate layer, and an innerliner. After the uncured tire has been built on a building drum, the uncured tire may be placed in a heated mold to shape it and heat it to vulcanization temperatures and, thereby, to produce a cured unitary tire from the multi-layers.

Vulcanization of the molded tire, typically, is carried out in heated presses under conditions well known to those skilled in the art.

Curing time will be affected by the thickness of the tire to be molded and the concentration and type of curing agent as well as the halogen content of the halogenated copolymer. However, the vulcanization parameters can readily be established with a few experiments utilizing, e.g., a laboratory characterization device well known in the art, the Monsanto Oscillating Disc Cure Rheometer (ODR, described in detail in American Society for Testing and Materials, Standard ASTM D 2084).

Tires produced according to the present invention offer black or white sidewall tire with the features of improved adhesion and ozone resistance as well as good curing and flex crack resistance. In the present tire, by using the halogenated copolymer in the tire sidewall, or in only the outer layer, good ozone resistance is

achieved. In addition, the outer layer acts as a barrier preventing migration of additives in protectants from the inner layer to the outside, thus eliminating the staining and discoloring problem discussed above.

The following examples are presented to illustrate the invention. All parts and percentages herein are by weight unless otherwise specified.

#### EXAMPLE 1

Master batches of brominated isobutylene/para-methylstyrene copolymers of varying bromination level, comonomer content and molecular weight were prepared. The copolymers had the properties listed in Table 1.

**TABLE 1**

	<b>COPOLYMER</b>					
<b>PROPERTY</b>	<b>EXXPRO 89-1</b>	<b>EXXPRO 93-4</b>	<b>EXXPRO 96-3</b>	<b>A</b>	<b>B</b>	<b>C</b>
<b>Para-Methylstyrene (wt%)</b>	5.0	7.5	7.5	9.5	13.6	13.6
<b>Bromomethylstyrene (mol%)</b>	0.75	1.2	0.75	1.0	1.0	0.8
<b>Mooney Viscosity (ML(1+8)125°C)</b>	35 ± 5	38 ± 5	40 ± 5	35 ± 5	38 ± 5	44 ± 5

Test compositions were compounded using 3-pass mixing conditions to blend the master batch components and the cure additives listed in Table 2. The compositions were cured at 150° C (18 minutes for tensile and fatigue testing; 21 minutes for Demattia and outdoor flex testing and 175° C (11 minutes for tensile and fatigue testing; 14 minutes for Demattia and outdoor flex testing).

TABLE 2

RECIPES	1A	1B	1C	1D	1E	1F	1G	1H
<b>Master Batch (phr)</b>								
EXXPRO 89-1	40							
EXXPRO 93-4		40						
EXXPRO 96-3			40					
Copolymer 1A				40			40	
Copolymer 1B					40			40
Copolymer 1C						40		
BUDENE 1207	50	50	50	50	50	50	50	50
SMR20	10	10	10	10	10	10	10	10
Black N660	40	40	40	40	40	40	40	40
FLEXON 641	12	12	12	12	12	12	12	12
ESCOREZ 1102	5	5	5	5	5	5	5	5
STRUCKOL 40MS	4	4	4	4	4	4	4	4
SP 1068	2	2	2	2	2	2	2	2
<b>Cure Package (phr)</b>								
Sulfur	0.40	0.40	0.40	0.40	0.40	0.40	0.80	0.80
Zinc Oxide	0.75	0.75	0.75	0.75	0.75	0.75	2.00	2.00
RYLEX 3011	0.60	0.60	0.60	0.60	0.60	0.60		
Stearic Acid	0.50	0.50	0.50	0.50	0.50	0.50		
MBTS	0.80	0.80	0.80	0.80	0.80	0.80		
TBBS							1.60	1.60
DURALINK HTS							2.00	2.00
SANTOVAR TAHQ							1.50	1.50
<b>TOTAL PHR</b>	166.05	166.05	166.05	166.05	166.05	166.05	170.9	170.9

The test compositions (1A through 1H) were tested for cure characteristics, tensile strength, flex fatigue, adhesion and ozone resistance. The results are presented in Table 3 below. The following descriptors are used herein to refer to cracking types and ratings:

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<u>Descriptor</u>	<u>Meaning</u>
Excel	No cracking
Good	Edge cracking only
Fair	Minor or Major cracking
Poor	Deep cracking, tear or separation
0	No cracking
1	Minor cracking
2	Major cracking
3	Deep Cracking
4	Tearing
5	Separated
6	Edge crack

10

15

TABLE 3

RECIPES	1A	1B	1C	1D	1E	1F	1G	1H
<b>Mooney Scorch @ 135°C</b>								
1 MU, min	7.5	6.3	8.0	8.6	8.4	8.3	1.8	5.9
2 MU, min	8.8	7.2	9.3	10.0	9.0	9.5	4.2	7.1
5 MU, min	11.	8.7	11.4	12.1	12.0	11.5	9.1	9.1
10 MU min	13.5	10.4	13.8	14.1	14.0	13.6	11.7	10.3
20 MU, min	16.7	12.8	16.0	16.6	17.0	16.6	14.2	11.2
<b>ODR @ 150°C, 1° Arc, 30 Min</b>								
ML, dNm	3.6	4.1	3.9	4.6	3.7	3.8	4.8	4.0
MH, dNm	14.3	18.1	15.1	19.6	16.0	14.1	18.3	19.2
ts2, min	7.6	5.8	7.7	6.8	7.7	8.1	7.4	5.7
t25, min	8.8	7.4	9.2	8.8	9.3	9.1	8.7	6.6
t50, min	13.5	10.7	14.1	13.1	13.5	13.6	12.3	9.1
t90, min	22.7	17.7	23.4	21.8	21.7	22.5	23.6	17.7
Peak Rate, dNm/min	1.5	1.4	0.8	1.1	1.0	0.9	1.2	2.1
Curve Type	SLM	P	SLM	SLM	SLM	P	M	P
<b>ODR @ 175°C, 1° Arc, 30 min</b>								
ML, dNm	4.0	4.1	4.2	4.0	3.8	4.1	4.0	4.1
MH, dNm	21.0	23.7	21.5	22.1	20.9	19.6	20.2	24.7
ts2, min	2.5	2.2	2.5	2.5	2.5	2.8	2.5	2.1
t25, min	3.1	2.8	3.2	3.2	3.1	3.4	2.9	2.5
t50, min	4.2	3.6	4.3	4.1	4.0	4.4	3.9	3.1
t90, min	7.8	8.7	7.8	7.2	6.8	8.1	9.0	6.3
Peak Rate, dNm/min	4.5	7.0	4.5	5.2	5.3	4.0	5.0	9.4
Curve Type	P	P	P	P	P	P	P	SLR
<b>Stress-Strain, Unaged, Tested @ RT, Cured @ 150°C</b>								
Stress @ break (MPa)	12.3	10.1	12.2	11.5	13.4	11.0	10.5	13.3
Stress @ 100% (MPa)	0.9	1.2	0.9	1.0	0.9	0.9	0.8	1.2
Stress @ 200% (MPa)	1.8	2.6	1.7	2.0	1.9	1.6	1.7	2.3
Stress @ 300% (MPa)	1.7	1.8	2.0	1.9	1.6	2.7	2.3	2.6
% Elongation @ break	776	603	831	752	789	808	799	752
Shore A @ 4 sec	38.1	41.5	38.9	40.5	39.3	37.7	36.3	43.1
<b>Stress-Strain, Unaged, Tested @ RT, Cured @ 175°C</b>								
Stress @ break (MPa)	13.1	11.9	13.1	14.0	12.8	12.8	12.9	10.2
Stress @ 100% (MPa)	1.1	1.4	1.1	1.2	1.0	1.0	0.9	1.3
Stress @ 200% (MPa)	2.1	3.0	2.1	2.6	2.1	2.0	1.8	6.2
Stress @ 300% (MPa)	3.6	5.0	3.6	4.2	3.6	3.3	3.0	4.2
% Elongation @ break	765	616	817	711	780	790	834	643
Shore A @ 4 sec	40.9	43.5	41.5	42.7	41.5	40.5	39.1	43.3

(Table 3 continued)

RECIPES	1A	1B	1C	1D	1E	1F	1G	1H
Pierced Demattia Flex, 300 Cycles/min, 60° bend, Unaged, Cured @ 175°C for 14 min								
Cycles	mm	mm	mm	mm	mm	mm	mm	mm
0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
4,500	3.1	3.5	3.3	3.4	3.3	3.3	3.2	5.3
9,000	3.6	4.4	3.4	3.6	3.5	3.8	3.6	8.0
13,500	3.9	4.7	4.0	4.2	5.1	3.9	4.1	9.6
18,000	4.2	5.0	4.1	4.4	5.6	4.5	4.2	10.5
36,000	5.1	6.4	4.8	5.0	7.5	5.6	4.8	14.0
54,000	6.2	8.3	5.2	5.5	8.4	6.5	5.4	16.0
72,000	6.4	7.8	6.0	5.7	8.7	7.1	5.9	18.1
90,000	7.4	8.2	6.4	6.1	10.0	7.4	6.2	19.8
378,000	11.0	8.4	7.8	7.0	13.0	11.8	7.6	25.0
810,000	11.1	8.5	8.0	8.8	14.0	12.4	9.0	25.0
1,242,000	11.1	8.5	8.2	9.0	14.6	12.9	10.0	25.0
1,674,000	12.7	8.5	8.2	10.7	15.1	13.0	9.8	25.0
2,200,000	12.8	8.7	8.2	10.7	15.1	13.0	10.4	25.0
Pierced Demattia Flex, 300 Cycles/min, 60° bend, Aged 70 Days, Cured @ 175°C for 14 min								
Cycles	mm	mm	mm	mm	mm	mm	mm	mm
0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
4,500	6.7	10.2	8.3	6.6	5.5	5.1	8.6	25.0
9,000	8.9	13.2	10.0	7.2	6.5	6.4	10.9	25.0
13,500	10.1	15.6	12.0	8.9	7.3	7.1	13.7	25.0
18,000	11.4	18.1	12.6	9.6	7.4	7.5	14.5	25.0
36,000	14.0	23.4	15.4	11.0	7.6	9.4	18.7	25.0
54,000	14.0	25.0	17.9	12.0	7.9	9.6	23.1	25.0
72,000	16.1	25.0	19.3	12.3	8.1	10.0	23.8	25.0
90,000	16.2	25.0	20.5	12.7	8.2	10.1	24.4	25.0
378,000	20.1	25.0	22.9	15.1	13.2	10.3	25.0	25.0
810,000	20.7	25.0	23.8	16.3	13.5	10.8	25.0	25.0
1,242,000	20.9	25.0	24.4	17.2	13.6	11.7	25.0	25.0
1,674,000	21.0	25.0	24.4	18.1	14.5	11.8	25.0	25.0
2,200,000	21.0	25.0	24.4	21.5	17.9	11.8	25.0	25.0
Fatigue-to-Failure, 101% Elong., 100 Cycles/min, Unaged, Tested @ RT, Cured @ 175°C for 14 min								
1	299469	474437	423700	568681	851035	249825	250295	503018
2	55249	323169	295957	489560	646772	206753	395717	495203
3	229232	272149	235538	524730	455105	262721	543253	608057
4	246140	378201	271244	662392	555320	213633	500604	671023
5	385646	358162	371391	576613	808128	253651	436442	591463
6	401886	434800	368917	727805	843489	255568	430599	596135
7	285398	471884	290089	834011	896678	368895	458971	605052
8	292774	417911	394821	848445	1E+06	273305	529245	814932
Mean, cycles	274474	391339	331457	654030	757741	260544	443141	610610
Rounded Off (x 1000)	275	391	332	654	758	261	443	611
Fatigue to Failure, 101% Elong., 100 Cycles/min, Aged 70 Days @ 70°C, Tested @ RT, Cured @ 175°C for 14 min								
1	514957	119872	77077	21566	12457	304584	193522	48003
2	632240	272194	619631	516511	187557	338433	251824	13264
3	459893	134145	295085	459893	404585	368364	296195	32935
4	556415	308092	677578	790353	623963	341525	293385	64726
5	663633	371743	496268	624169	791603	545887	398263	39982
6	590643	359202	375256	433444	721574	564278	527785	74095
7	402796	367100	681192	686172	915044	367767	503897	6491
8	570675	311924	510982	774470	1E+06	688728	605345	9490
Mean, cycles	548907	280534	466634	538322	584184	439946	383777	36123
Rounded Off (x 1000)	549	281	467	538	584	440	384	36

(Table 3 continued)

[illegible]

(Table 3 continued)

[illegible]

(Table 3 continued)

RECIPE	1A	1B	1C	1D	1E	1F	1G	1H
<b>Outdoor Flex, Unaged, Cured @ 175°C for 14 min</b>								
Crack 1, days/Type of Crack	8/1	19/6	8/1	0	0	19/6	8/1	3/1
Crack 2, days/Type of Crack	12/1/6		18/2/6			20/1/6	18/1/6	19/1/6
Crack 3, days/Type of Crack	18/2/6		23/3/6				21/2/6	23/1/6
Crack 4, days/Type of Crack	23/3/6							
Test Duration/Days	26	26	26	26	26	26	26	26
Rating	Poor	Good	Poor	Excel	Excel	Good	Fair	Good
<b>Outdoor Flex, Aged 70 Days @ 70°C, Cured @ 175°C for 14 min</b>								
Crack 1, days/Type of Crack	24/1/6	27/6	21/6	27/1/6	0	27/6	27/1	15/6/2
Crack 1, days/Type of Crack			24/1/6				30/2	21/4/6
Crack 1, days/Type of Crack							37/2/6	33/5
Crack 1, days/Type of Crack								
Test Duration/Days	37	37	37	37	37	37	37	37
Rating	Fair	Good	Fair	Fair	Excel	Good	Fair	Poor

Blends 1D through 1H exhibited similar cure characteristics to blends 1A, 1B and 1C and similar tensile properties. Blends 1D and 1F had better fatigue-to-failure and flex crack propagation resistance, and comparable ozone resistance.

## EXAMPLE 2

Blends of rubber with a high-bromine, low para-methylstyrene copolymer and a low-bromine, high para-methylstyrene copolymer were prepared at varying ratios. The high-bromine, low para-methylstyrene copolymer was EXXPRO 93-4 copolymer comprised of 7.5 weight percent para-methylstyrene and 1.2 mole percent benzylic bromine. It had a Mooney viscosity ML (1+8) at 125° C of  $38 \pm 5$ . The low-bromine, high para-methylstyrene copolymer (Copolymer 2) was comprised of 13.6 weight percent para-methylstyrene and 0.56 mole percent benzylic bromine (0.78 weight percent bromine). It has a Mooney viscosity ML (1 + 8) at 125° C of  $37 \pm 5$ . The blends were compounded as described in Example 1 and cured at 180° C for 15 minutes. The blends had the compositions of Table 4.

TABLE 4

RECIPES	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Master Batch														
EXXPRO 93-4	35	40	45	50	55	60	65	35	40	45	50	55	60	65
Copolymer 2														
BUDENE	54.17	50	45.83	41.67	37.5	33.33	29.17	54.17	50	45.83	41.67	37.5	33.33	29.17
1207														
SMR 20	10.83	10	9.17	8.33	7.5	6.67	5.83	10.83	10	9.17	8.33	7.5	6.67	5.83
N351	40	40	40	40	40	40	40	40	40	40	40	40	40	40
FLEXON 641	12	12	12	12	12	12	12	12	12	12	12	12	12	12
STRUCKTOL	4	4	4	4	4	4	4	4	4	4	4	4	4	4
40MS														
ESCOREZ	5	5	5	5	5	5	5	5	5	5	5	5	5	5
1102														
SP 1068	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Cure Package														
Stearic Acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Zinc Oxide	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
RYLEX 3011	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
MBTS	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
TOTAL PHR	166.05	166.05	166.05	166.05	166.05	166.05	166.05	166.05	166.05	166.05	166.05	166.05	166.05	166.05

The blends were evaluated for cure characteristics, tensile and hardness properties, flex crack propagation resistance, tensile fatigue-to-failure, static and dynamic ozone resistance, and outdoor flex resistance. The results are presented in Table 5 using the same descriptor meanings as in Table 3.

TABLE 5

RECIPES	2A	2B	2C	2D	2E	2F	2G	2H	2I	2J	2K	2L	2M	2N
Mooney Viscosity @ 100°C														
ML1+4min (MU)		45.3	42.9	44.7	43.5	43.7	44.6	45.0	44.9	43.7	44.2	43.5	44.4	44.4
ML1+8min(MU)	42.4	43.6	41.2	43.4	42.2	42.1	43.2	43.4	43.5	42.3	42.6	42.0	42.9	43.2
Mooney Scorch @ 135°C														
5 MU, MIN	12.8	12.2	12.2	12	12.4	12.8	12.3	16	15.5	15.1	15.4	15.4	14.5	14.2
10 MU, min	14.7	13.8	13.8	13.5	13.8	14.2	13.7	18.9	18.3	17.7	17.6	17.8	16.6	16.3
MDR @ 160°C, 5° Arc, 60 min														
ML, dNm	1.35	1.37	1.32	1.37	1.32	1.27	1.27	1.46	1.44	1.39	1.38	1.34	1.37	1.38
MI, dNm	8.67	9.03	9.27	10.08	10.21	10.33	10.74	7.89	7.73	7.7	7.44	7.22	7.33	7.29
Max-Min, dNm	7.32	7.66	7.94	8.71	8.88	9.06	9.46	6.36	6.29	6.28	6.06	5.87	5.95	5.90
t2, min	4.92	4.55	4.51	4.34	4.29	4.31	4.22	5.34	5.20	5.16	5.19	5.06	4.99	4.92
t25, min	4.72	4.46	4.49	4.50	4.47	4.52	4.50	4.80	4.67	4.63	4.59	4.38	4.33	4.26
t50, min	6.72	6.36	6.35	6.28	6.26	6.26	6.28	6.82	6.61	6.54	6.46	6.25	6.24	6.14
t90, min	21.99	20.45	19.67	17.49	17.15	15.52	14.70	14.55	14.14	14.06	13.69	13.61	15.18	14.83
Peak Rate, dNm/min	1.00	1.20	1.20	1.40	1.40	1.50	1.50	0.90	1.00	1.00	0.90	0.90	0.90	0.90
Curve Type	SLM	SLM	SLM	P	P	P	P	P	P	P	P	P	P	P
MDR @ 180°C, 5° Arc, 30 min														
ML, dNm	1.16	1.19	1.17	1.21	1.17	1.12	1.08	1.22	1.20	1.16	1.21	1.16	1.13	1.10
MI, dNm	8.11	8.91	9.33	10.06	10.38	10.66	10.90	7.12	7.18	7.26	7.52	7.36	7.29	7.05
Max-Min, dNm	6.95	7.73	8.16	8.86	9.21	9.54	9.83	5.90	5.98	6.10	6.32	6.21	6.16	5.95
t2, min	1.72	1.69	1.57	1.55	1.57	1.59	1.65	1.87	1.83	1.81	1.69	1.69	1.74	1.76
t25, min	1.64	1.68	1.59	1.59	1.63	1.68	1.76	1.65	1.63	1.63	1.55	1.55	1.58	1.59
t50, min	2.14	2.16	2.05	2.05	2.09	2.17	2.32	2.25	2.22	2.19	2.07	2.05	2.1	2.11
t90, min	4.18	4.20	3.94	3.97	4.09	4.18	4.63	4.23	4.14	4.05	3.83	3.76	4.02	3.98
Peak Rate, dNm/min	3.60	4.10	4.60	5.00	5.20	5.20	4.70	2.60	2.70	2.90	3.20	3.20	3.00	2.90
Curve Type	P	P	SLR	P	P	P	P	SLR	SLR	SLR	SLR	SLR	SLR	P
Stress-Strain Unaged, Tested @ RT, Cured @ 150°C														
Stress @ break (MPa)	12.23	13.09	11.66	12.19	11.48	11.93	11.15	14.35	14.35	15.62	15.35	13.97	14.40	13.85
Stress @ 100% (MPa)	1.42	1.63	1.68	1.89	2.19	2.30	2.79	1.00	1.00	1.09	1.15	1.16	1.29	1.35
Stress @ 135% (MPa)	1.99	2.32	2.36	2.73	3.21	3.52	4.13	1.29	1.29	1.44	1.51	1.53	1.74	1.81
Stress @ 200% (MPa)	3.36	3.95	3.89	4.72	5.42	5.94	6.83	2.09	2.09	2.35	2.49	2.46	2.87	2.92
Stress @ 300% (MPa)	6.00	6.92	6.89	8.12	8.86	9.61	10.71	3.83	3.83	4.29	4.48	4.39	5.05	5.00
% Elongation @ break	533	509	462	421	377	376	211	764	808	807	761	727	717	700
Shore A @ 4 sec.	48.3	49.9	49.9	49.9	51.3	52.3	52.9	42.7	43.3	44.1	43.9	45.5	45.3	45.5

(Table 5 continued)

RECIPE	2A	2B	2C	2D	2E	2F	2G	2H	2I	2J	2K	2L	2M	2N
Pierced Demattia Flex, 300 Cycles/min, 60° bend.														
CYCLES														
0	2.00	2.0	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
1,500	4.10	4.10	5.10	6.60	7.95	10.70	11.80	3.50	3.10	3.10	3.20	3.20	3.20	3.40
3,000	4.70	4.70	6.30	8.60	10.00	13.50	16.40	3.70	3.50	3.50	3.50	3.50	3.50	3.50
4,500	4.80	5.40	6.50	9.50	10.35	15.85	20.70	3.90	3.80	3.80	3.80	3.80	3.80	3.80
6,000	5.50	6.20	7.60	9.85	11.15	17.45	23.90	3.90	3.90	3.90	3.90	3.90	3.90	3.90
7,500	5.70	6.45	8.10	11.00	12.30	19.15	25.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
9,000	6.00	6.75	8.20	11.15	13.25	20.75	25.00	4.10	4.10	4.10	4.10	4.10	4.10	4.10
13,500	6.55	7.55	10.10	12.50	14.60	23.90	25.00	4.20	4.20	4.20	4.20	4.20	4.20	5.00
18,000	6.90	8.05	11.10	13.40	15.95	24.55	25.00	5.60	4.70	5.00	5.25	6.80	6.75	6.75
36,000	7.70	9.75	13.20	15.55	19.65	25.00	25.00	5.60	4.70	5.00	5.25	6.80	6.75	6.75
54,000	8.10	10.85	14.30	16.50	22.95	25.00	25.00	5.75	4.80	5.90	5.85	8.05	7.40	7.95
72,000	8.95	11.60	15.70	18.10	24.20	25.00	25.00	6.00	5.00	6.50	6.55	8.45	7.90	8.15
90,000	9.35	11.80	17.00	19.85	24.35	25.00	25.00	6.05	5.15	6.85	6.60	9.05	8.20	8.85
378,000	10.05	11.90	22.80	20.85	24.90	25.00	25.00	6.05	5.15	7.05	6.60	11.65	10.50	12.15
847,165	15.60	12.40	25.00	22.00	25.0	25.00	25.00	8.25	5.20	7.05	7.15	16.90	11.05	14.55
1,242,000	15.70	12.50	25.00	22.25	25.00	25.00	25.00	8.25	5.20	7.30	7.35	17.10	12.05	15.05
2,200,000	16.10	12.50	25.00	22.25	25.00	25.00	25.00	8.35	5.20	7.35	7.45	17.50	14.90	15.80
Fatigue-to-Failure, 101% Elong., 100 Cycles/min, Unaged, Tested @ RT, Cured @ 180°C for 15 min														
1	382,098	155446	106195	142066	89762	194773	109250	692186	131425	366569	415308	744755	>1M	>1M
2	348919	107814	105536	71838	117265	63778	111594	692914	290035	338539	293552	62931	>1M	>1M
3	393855	110177	53523	342040	53111	70859	17893	536780	168475	326686	543833	268469	>1M	>1M
4	357880	101538	62925	131567	58382	39272	82772	809775	411101	319488	557428	1032000	>1M	>1M
5	448392	81502	902147	236514	142532	96451	27533	737100	551878	263500	716738	1679504	>1M	>1M
6	554181	286427	166066	469875	282887	142961	25545	1358755	763175	349740	562505	1143315	>1M	>1M
7	569631	307435	161290	57740	276731	152161	76609	1797677	603086	435001	880249	1865972	>1M	>1M
8	562373	320560	130784	570482	567069	327414	110034	1504745	244402	504176	689401	673777	>1M	>1M
Mean	452166	183862	211058	252765	198467	123459	70154	1016242	395447	362962	582377	937590	>1M	>1M
Rounded Off (x 1000)	452	184	211	253	199	124	70	>1M	395	363	582	938	>1M	>1M
Ozone Static - Bent Loop @ 40°C & 25 ppm of O3														
Crack 1, Days/Type of Crack	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Test Duration/Days	31	31	31	31	31	31	31	31	31	31	31	31	31	31
Rating	Excel	Excel	Excel	Excel	Excel	Excel	Excel	Excel	Excel	Excel	Excel	Excel	Excel	Excel

(Table 5 continued)

RECIPE	2A	2B	2C	2D	2E	2F	2G	2H	2I	2J	2K	2L	2M	2N
Ozone Dynamic - Tensile @ 40°C & 25 ppm of O <sub>3</sub>														
Crack 1, Days/Type of Crack	17.4	0	0	0	0	0	0	7.4	0	0	0	0	0	0
Crack 2, Days/Type of Crack	26.5	0	0	0	0	0	0	13.5	0	0	0	0	0	0
Test Duration/Days	31	31	31	31	31	31	31	31	31	31	31	31	31	31
Rating	Poor	Excel	Excel	Excel	Excel	Excel	Excel	Poor	Excel	Excel	Excel	Excel	Excel	Excel
Outdoor Flex														
Crack 1, Days/Type of Crack	10.1	24.6	0	0	0	0	0	4.2	10.1	24.1	24.1	24.1	24.1	24.1
Crack 2, Days/Type of Crack	28.1/6	31.1/6	0	0	0	0	0	7.2/6	21.2	0	0	0	0	0
Crack 3, Days/Type of Crack	0	0	0	0	0	0	0	10.3/6	38.3	0	0	0	0	0
Crack 4, Days/Type of Crack	0	0	0	0	0	0	0	0	31.3/6	0	0	0	0	0
Test Duration/Days	41	41	41	41	41	41	41	41	41	41	41	41	41	41
Rating	Fair	Fair	Excel	Excel	Excel	Excel	Excel	Poor	Poor	Poor	Fair	Fair	Fair	Fair

These results show that blends with Copolymer 2 had cure characteristics comparable or slightly better than blends with the EXXPRO 93-4, better tensile properties, comparable hardness, substantially better flex crack propagation resistance, better fatigue-to-failure, and better static and dynamic ozone resistance.

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### EXAMPLE 3

Master batches of brominated isobutylene/para-methylstyrene copolymers of varying bromination level, comonomer content and molecular weight were prepared. The copolymers had the properties listed in Table 6.

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**TABLE 6**

PROPERTY	COPOLYMER		
	EXXPRO 90-10	Test 1	Test 2
Para-Methylstyrene (wt%)	7.5	10.0	12.5
Bromomethylstyrene (mol%)	1.2	0.96	0.84
Mooney Viscosity (ML(1+8)125°C)	45 ± 5	39 ± 5	46 ± 5

Test compositions were compounded to blend the master batch components and the cure additives listed in Table 7. Three-pass mixing conditions were used for samples 1W, 1X and 1Y. Two-pass mixing conditions were used for sample 1Z. BUDENE™ 1207 is a trademarked butadiene rubber available from Goodyear. FLEXON 641 is a naphthenic petroleum oil. FLEXON 815 is a paraffinic petroleum oil.

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**TABLE 7**

<b>RECIPES</b>	<b>1W</b>	<b>1X</b>	<b>1Y</b>	<b>1Z</b>
<b>Master Batch (phr)</b>				
EXXPRO 90-10	40.00			
Test 1		50.00		
Test 2			50.00	
BUDENE 1207	50.00	41.67	41.67	50.00
SMR	10.00	8.33	8.33	50.00
Black N330	55.00	40.00	40.00	
Black N660				50.00
FLEXON 641		12.00	12.00	10.00
FLEXON 815	12.00			
STRUKTOL 40MS	5.00	4.00	4.00	
ESCOREZ 1102	3.00	5.00	5.00	5.00
SP 1068	3.00	2.00	2.00	
6PPD				3.00
TMQ				1.00
Sunolite 240				3.00
<b>Cure Package (phr)</b>				
Stearic Acid	1.00	0.50	0.50	2.00
Zinc Oxide	1.00	0.75	0.75	3.00
Sulfur	0.32	0.40	0.40	1.00
RYLEX 3011	0.50	0.60	0.60	
MBTS	1.50	0.80	0.80	
DHT4A2	0.50			
TBBS				2.00
<b>TOTAL PHR</b>	<b>182.82</b>	<b>166.05</b>	<b>166.05</b>	<b>180.00</b>

The test compositions (1W through 1Z) were tested for cure characteristics, tensile strength, flex fatigue, adhesion and ozone resistance. The results are presented in Table 8.

TABLE 8

PROPERTIES	1W	1X	1Y	1Z
<b>Mooney Viscosity 1+4 @ 100°C</b>	74	55	58	51
<b>Mooney Scorch @ 121°C</b>				
5 MU, min	23.4	30.7	30.2	30.7
10 MU, min	28.4	35.7	35.2	35.7
<b>MDR @ 180°C, 0.5° Arc</b>				
ML, dNm	1.88	1.00	1.18	1.48
MH, dNm	11.31	8.17	7.63	11.12
ts2, min	1.45	1.89	1.88	1.31
t25, min	1.57	1.83	1.75	1.39
t50, min	2.14	2.35	2.30	1.68
t90, min	3.50	4.49	4.38	2.26
Peak Rate, dNm./min				
Curve Type				
<b>Stress-Strain, Unaged, Tested @ RT, Cured @ 180°C</b>				
Time of Cure (min)	7.0	7.0	7.0	5.0
Stress @ break (MPa)	15.9	11.6	12.7	16.4
Stress @ 100% (MPa)	1.9	1.5	1.4	1.3
Stress @ 300% (MPa)	7.8	6.0	5.1	6.6
% Elongation @ break	580	509	639	556
Shore A	54.0	45.0	43.0	46.0
<b>Outdoor Flex @ 672 hours, 0=Broken; 10=No cracks</b>	4	9	10	7
<b>Pierced Demattia Flex @ 1,307,890 cycles</b>	12.75	16.10	8.15	7.40
<b>Fatigue-to-Failure, 101% Elong., 100 Cycles/min, Unaged, Tested @ RT</b>	73,706	72,137	215,166	378,980
<b>Die B Tear @ 100°C</b>	238	72	101	147
<b>Die C Tear @ 100°C</b>	188	93	101	143
<b>1" Strip Adhesion to "Carcass" Tested @ 100°C</b>				
Avg. Peak (lb)	91	93	115	118
Surface Appearance	T	P	P	P
<b>1" Strip Adhesion to "Self" Tested @ 100°C</b>				
Avg. Peak (lb)	69	100	127	112
Surface Appearance	T	P	P	P
<b>Dynamic Ozone, 50 pphm, 60% Extension, Hrs. to First Crack</b>	<24; <24	<48; <48	NC@336; 336	<48; <48

5 Blends 1X and 1Y exhibited superior outdoor flex and ozone resistance over blends 1W and 1Z. The test compositions (1W through 1Z) were used to re-side tires. Tests were conducted on the tires to measure wear and ozone resistance. The results are presented in Table 9.

**TABLE 9**

<b>PROPERTIES</b>	<b>1W</b>	<b>1X</b>	<b>1Y</b>	<b>1Z</b>
<b>5% Deflection, 18,550 miles</b>				
Cracking	none	none	none	slight
Color	good	good	good	brown bloom
<b>10% Deflection, 18,500 miles</b>				
Cracking	none	none	none	slight
Color	moderate stain	good	good	brown bloom
<b>Flexsys Ozone Wheel Test, 500 hours, 10=no cracks, 0=failure</b>	6	8	10	6

- 5 Blends 1X and 1Y exhibited superior wear characteristics to blends 1W and 1Z. Blends 1X and 1Y also exhibited superior ozone resistance over blends 1W and 1Z.

CLAIMS

1. A blend of rubber and a copolymer of an isoolefin, para-alkylstyrene and bromoalkylstyrene, wherein the copolymer comprises at least 9.5 but less than 20 weight percent of styrenics, and at least 0.2 but less than 1 mole percent bromoalkylstyrene.
2. The blend of claim 1 wherein the copolymer comprises from 35 to 65 weight parts per hundred parts of total rubber.
3. The blend of claim 1 wherein said styrenics comprise either para-alkylstyrene, brominated para-alkylstyrene, alpha-methylstyrene, brominated alpha-methylstyrene or combinations thereof.
4. The blend of claim 1 wherein the isoolefin is isobutylene and the bromoalkylstyrene is para-bromomethylstyrene.
5. The blend of claim 1 wherein the rubber is selected from the group consisting of natural rubber, styrene-butadiene rubber, polybutadiene rubber, polyisoprene rubber and combinations thereof.
6. The blend of claim 1 wherein the copolymer comprises from 12 to 17 weight percent styrenics and from 0.4 to 0.8 mole percent bromoalkylstyrene.
7. A blend of from 35 to 65 parts by weight of a rubber selected from the group consisting of natural rubber, styrene-butadiene rubber, polybutadiene rubber, polyisoprene rubber and combinations thereof, and from 35 to 65 parts by weight of a copolymer of isobutylene, from 9.5 up to 20 weight percent para-methylstyrene and from 0.2 to 1 mole percent para-bromomethylstyrene.
8. The blend of claim 7 wherein the copolymer comprises from 12 to 17 weight percent para-methylstyrene and from 0.4 to 0.8 mole percent para-bromomethylstyrene.
9. A tire sidewall comprising the blend of claim 1.

10. A tire sidewall comprising:

- a) an outer layer comprising the blend of claim 1; and
- b) an inner layer comprising a highly unsaturated rubber or blend of unsaturated rubbers.

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11. A multi-layered tire sidewall comprising:

- a) an outer layer comprising a blend of an unsaturated rubber and a copolymer of an isoolefin and a para-alkylstyrene, and
- b) an inner layer optionally comprising a highly unsaturated rubber or blend of unsaturated rubbers,

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wherein the copolymer comprises from 9.5 to 20 weight percent aromatic monomers and from 0.2 to 1.0 mole percent para-bromoalkylstyrene.

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12. The blend of claim 1 wherein the quantities of said bromoalkylstyrene and said para-alkylstyrene satisfy the following formula:

$$X = [1.91 - (0.094 \times Y)] \pm 0.1$$

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wherein "X" is mole percent bromoalkylstyrene and "Y" is weight percent para-alkylstyrene (between the limits of 9.5 to 20 weight percent).

13. The blend of claim 12 wherein said bromoalkylstyrene is para-bromomethylstyrene and said para-alkylstyrene is para-methylstyrene.

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14. The blend of claim 13 wherein the mole percent para-bromomethylstyrene is 0.96 and the weight percent para-methylstyrene is 10.

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15. The blend of claim 13 wherein the mole percent para-bromomethylstyrene is 0.84 and the weight percent para-methylstyrene is 12.5.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 98/08863

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L21/00 C08L23/28 B60C1/00 //(C08L21/00,23:28),  
(C08L23/28,21:00)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L B60C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 92 03302 A (EXXON CHEMICAL PATENTS INC) 5 March 1992 cited in the application see claims 14,23 ---	1-9, 12-15
X	EP 0 738 754 A (BRIDGESTONE CORP) 23 October 1996 see claim 2 ---	1-8, 12-15
X	US 5 504 164 A (O'DONNELL KEVIN) 2 April 1996 see column 4, line 24 - line 25; claim 1 ---	1-8, 12-15
A	US 5 376 438 A (COSTEMALLE BERNARD ET AL) 27 December 1994 cited in the application see column 2, line 43 - line 68; claim 16 -----	1-15

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

24 August 1998

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03/09/1998

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# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

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